

[Document Name] Request for Patent Application

[Reference Number] K01934PP00

[Date of Submission] October 22nd, 2002

[Addressee] Commissioner of Patent Office

5 [International Patent classification] C08L 53/02

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[Deposit Number] 008198

[Amount Paid] 21000 JP yen

25 [List of Submitted Items]

[Name of Item]	Specification 1
[Name of Item]	Abstract 1
[Request for Proof]	Yes

[Document Name] SPECIFICATION

[Title of the Invention] POLYOLEFIN-BASED RESIN COMPOSITION  
AND USE THEREOF

[Claims]

5 [Claim 1] A polyolefin-based resin composition, comprising an  
addition polymerization-based block copolymer (I) and a  
polyolefin-based resin (II), wherein:

the addition polymerization-based block copolymer (I)  
comprises at least one polymer block A and at least one  
10 polymer block B, the polymer block A essentially comprising an  
aromatic vinyl compound containing at least 1% by mass of an  
alkylstyrene-derived structural unit (a) in which at least one  
alkyl group having 1 to 8 carbon atoms is bound to a benzene  
ring, the polymer block B essentially comprising a conjugated  
15 diene compound;

at least the part of the addition polymerization-based  
block copolymer (I) formed of the polymer block A comprises at  
least one selected from the group consisting of block  
copolymers that can undergo crosslinking upon exposure to an  
20 active energy ray and hydrogenated products thereof; and

after molded into a desired shape, the composition is  
exposed to an active energy ray to carry out the crosslinking  
reaction.

[Claim 2] The polyolefin-based resin composition according to  
25 claim 1, wherein the alkylstyrene-derived structural unit (a)

in which at least one alkyl group having 1 to 8 carbon atoms is bound to a benzene ring is a p-methylstyrene unit.

[Claim 3] The polyolefin-based resin composition according to claim 1 or 2, wherein the active energy ray is an electron beam.

[Claim 4] The polyolefin-based resin composition according to any one of claims 1 to 3, further containing a photopolymerization initiator.

[Claim 5] A molded article obtained from the polyolefin-based resin composition according to any one of claims 1 to 4.

[Claim 6] A laminate comprising a layer formed of the polyolefin-based resin composition according to any one of claims 1 to 4.

[Detailed Description of the Invention]

[0001]

[Technical Field of the Invention]

The present invention relates to a polyolefin-based resin composition. The polyolefin-based resin composition of the present invention is flexible, yet exhibits heat resistance, mechanical properties, and solvent resistance in a well-balanced manner, and is thus suitable for use in wire coatings, coatings of various cables, tubes, films, and various other applications.

[0002]

[Prior Art]

Polyolefin-based resins generally show moderate heat resistance as well as high flexibility and high solvent resistance. This feature makes the compounds suitable for use in a wide range of applications, including wire coatings; cable coatings; tubes; films, such as laminate films, agricultural films, stretch wrapping films, adhesive films, and medical films; sheets, such as agricultural sheets; processed paper; injection molding; pipes; bundling tapes; flat yarns; and fibers. Nonetheless, as far as such applications as wire coatings, tubes, films, and sheets are concerned, further improvements are required in certain physical properties of polyolefin-based resins, including heat resistance and solvent resistance.

Several methods have been proposed in an effort to impart required mechanical properties, heat resistance and solvent resistance to the polyolefin-based resins. In one such method, a crosslinkable polymer composition composed of a polyolefin-based resin and a crosslinkable monomer is exposed to an active energy ray (See, Patent Document 1). In another method, polyethylene is blended with an ethylene- $\alpha$ -olefin copolymer or a styrene-based block copolymer (See, Patent Document 2).

[0003]

[Patent Document 1]

Japanese Patent Laid-Open Publication No. Hei 10-147671  
[Patent Document 2]

Japanese Patent Laid-Open Publication No. Hei 11-130921

[0004]

However, the method of Patent Document 1, which involves addition of a crosslinkable monomer and irradiation with an active energy ray, cannot necessarily provide the resulting crosslinkable polymer composition with sufficient heat resistance or solvent resistance. In the method of Patent Document 2, in which a polyethylene is mixed with an ethylene- $\alpha$ -olefin copolymer or a styrene-based block copolymer, the addition of ethylene- $\alpha$ -olefin copolymer does not significantly improve the heat resistance of the resulting resin, while the addition of styrene-based block copolymer often results in a reduced solvent resistance of the resin. Thus, the method is not appropriate when it is desired to obtain a composition that exhibits flexibility and heat resistance in a well-balanced manner. For these reasons, a demand exists for a resin composition that not only has flexibility, but also exhibits mechanical strength, heat resistance, and solvent resistance in a well-balanced manner when used in applications such as wire coatings, tubes and films.

[0005]

[Problem to be Solved by the Invention]

In view of the above-described drawbacks of conventional technologies, it is an objective of the present invention to provide a polyolefin-based resin composition that has

flexibility while exhibiting mechanical strength, heat resistance, and solvent resistance in a well-balanced manner.  
[0006]

[Means for Solving the Problem]

5           The present invention achieves this objective by providing the following:

          (1) A polyolefin-based resin composition, comprising an addition polymerization-based block copolymer (I) and a polyolefin-based resin (II), wherein:

10           the addition polymerization-based block copolymer (I) comprises at least one polymer block A and at least one polymer block B, the polymer block A essentially comprising an aromatic vinyl compound containing at least 1% by mass of an alkylstyrene-derived structural unit (a) (which may be  
15   referred to simply as "structural unit (a)" hereinafter) in which at least one alkyl group having 1 to 8 carbon atoms is bound to a benzene ring, the polymer block B essentially comprising a conjugated diene compound unit;

          at least the part of the addition polymerization-based  
20   block copolymer (I) formed of the polymer block A comprises at least one selected from the group consisting of block copolymers that can undergo crosslinking upon exposure to an active energy ray and hydrogenated products thereof; and

          after molded into a desired shape, the composition is  
25   exposed to an active energy ray to carry out the crosslinking

reaction.

(2) The polyolefin-based resin composition according to (1) above, wherein the alkylstyrene-derived structural unit (a) in which at least one alkyl group having 1 to 8 carbon atoms is bound to a benzene ring is a p-methylstyrene unit.

(3) The polyolefin-based resin composition according to (1) or (2) above, wherein the active energy ray is an electron beam.

(4) The polyolefin-based resin composition according to any one of (1) to (3) above, further containing a photopolymerization initiator.

(5) A molded article obtained from the polyolefin-based resin composition according to any one of (1) to (4) above.

(6) A laminate comprising a layer formed of the polyolefin-based resin composition according to any one of (1) to (4) above.

[0007]

[Preferred Embodiments of the Invention]

The present invention will now be described in further detail.

The addition polymerization-based block copolymer (I) for forming the polyolefin-based resin composition of the present invention includes at least one polymer block A and at least one polymer block B. The polymer block A essentially comprises an aromatic vinyl compound that contains at least 1% by mass



of an alkylstyrene-derived structural unit (a) in which at least one alkyl group having 1 to 8 carbon atoms is bound to a benzene ring. The polymer block B essentially comprises a conjugated diene compound unit. At least the part of the addition polymerization-based block copolymer (I) formed of the polymer block A comprises at least one selected from the group consisting of block copolymers that can undergo crosslinking upon exposure to an active energy ray and hydrogenated products thereof.

10 [0008]

Examples of alkylstyrenes for forming the structural unit (a) of the polymer block A include o-alkylstyrene, m-alkylstyrene, p-alkylstyrene, 2,4-dialkylstyrene, 3,5-dialkylstyrene, and 2,4,6-trialkylstyrene with their alkyl groups having 1 to 8 carbon atoms, and halogenated alkylstyrenes in which one or more of the hydrogen atoms borne by the alkyl groups of the alkylstyrenes have been substituted with halogen atoms. Specific examples of the alkylstyrenes for forming the structural unit (a) include o-methylstyrene, m-methylstyrene, p-methylstyrene, 2,4-dimethylstyrene, 3,5-dimethylstyrene, 2,4,6-trimethylstyrene, o-ethylstyrene, m-ethylstyrene, p-ethylstyrene, 2,4-diethylstyrene, 3,5-diethylstyrene, 2,4,6-triethylstyrene, o-propylstyrene, m-propylstyrene, p-propylstyrene, 2,4-dipropylstyrene, 3,5-dipropylstyrene, 2,4,6-tripropylstyrene, 2-methyl-4-

ethylstyrene, 3-methyl-5-ethylstyrene, o-chloromethylstyrene,  
m-chloromethylstyrene, p-chloromethylstyrene, 2,4-  
bis(chloromethyl)styrene, 3,5-bis(chloromethyl)styrene, 2,4,6-  
tri(chloromethyl)styrene, o-dichloromethylstyrene, m-  
5 dichloromethylstyrene, and p-dichloromethylstyrene.

[0009]

The polymer block A may contain one or more units of the  
above-described alkylstyrenes and halogenated alkylstyrenes  
for forming the structural unit (a). Of these, p-methylstyrene  
10 unit, which can readily undergo crosslinking and is readily  
available, is particularly preferred as the structural unit  
(a).

[0010]

Examples of the aromatic vinyl compound units other than  
15 those for forming the structural unit (a) include those formed  
of styrene,  $\alpha$ -methylstyrene,  $\beta$ -methylstyrene, monofluorostyrene,  
difluorostyrene, monochlorostyrene, dichlorostyrene,  
methoxystyrene, vinyl naphthalene, vinylanthracene, indene, and  
acetonaphthylene. Of these, styrene and  $\alpha$ -methylstyrene are  
20 particularly preferred.

[0011]

The polymer block A of the addition polymerization-based  
block copolymer (I) forms hard segments of the thermoplastic  
elastomer. The alkyl groups, which are each bound to a benzene  
25 ring to form the structural unit (a), serve to introduce cross

linkages in the hard segments of the polymer block A as they undergo the static crosslinking reaction upon exposure to an active energy ray.

[0012]

5       The proportion of the structural unit (a) in the polymer block A is 1% by mass or more and, preferably, 10% by mass or more, and more preferably 40% by mass or more with respect to the mass of the polymer block A. The polymer block A may be made entirely of the structural unit (a). If the proportion of  
10   the structural unit (a) is less than 1% by mass, then the cross linkages are not introduced into the polymer block A to a sufficient degree, resulting in insufficient mechanical strength of the resulting polyolefin-based resin composition. In the polymer block A, the structural unit (a) and other  
15   aromatic vinyl compound units may be linked to one another either randomly, in blocks, in taper or in tapered blocks.

[0013]

Preferably, the polymer block A is present in the addition polymerization-based block copolymer (I) in an amount  
20   of 10 to 40% by mass. If the amount of the polymer block A is less than 10% by mass, then insufficient crosslinking results, leading to insufficient heat resistance and mechanical properties. If the amount of the polymer block A is greater than 40% by mass, then the resulting polyolefin-based resin  
25   composition does not show sufficient flexibility.

[0014]

When necessary, the polymer block A may include, along with the structural unit composed of the aromatic vinyl compound containing the structural unit (a), a small amount of structural units composed of other polymerizable monomers. The proportion of the structural unit composed of such other polymerizable monomers is preferably 30% by mass or less and, more preferably, 10% by mass or less based on the mass of the polymer block A. Examples of the other polymerizable monomers include 1-butene, pentene, hexene, butadiene, isoprene, and methyl vinyl ether.

[0015]

Aside from the polymer block A composed of the aromatic vinyl compound unit containing the structural unit (a), the addition polymerization-based block copolymer (I) for use in the present invention may contain a polymer block composed of an aromatic vinyl compound that does not contain the structural unit (a).

[0016]

Examples of the conjugated diene compounds to form the polymer block B of the addition polymerization-based copolymer (I) include butadiene, isoprene, 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene, and 1,3-hexadiene or the like. The polymer block B may be composed solely of one of these compounds, or it may be composed of two or more of the compounds. The

polymer block B is preferably composed of butadiene, isoprene,  
or a mixture of butadiene and isoprene. The polymer block B  
may have any microscopic structure, which may be present in  
any amount. When two or more of these compounds are used, they  
5 may be linked to one another either randomly, taperedly, in  
partial blocks, or in combination of two or more of these  
manners of linking.

[0017]

When necessary, the polymer block B may contain, along  
10 with the structural unit composed of the conjugated diene  
compound, a small amount of structural units composed of other  
polymerizable monomers. The proportion of such other  
polymerizable monomers is preferably 30% by mass or less and,  
more preferably, 10% by mass or less based on the total mass  
15 of the polymer block B that forms the addition polymerization-  
based block copolymer (I). Examples of the other polymerizable  
monomers include styrene,  $\alpha$ -methylstyrene, and the  
aforementioned alkylstyrenes for forming the structural unit  
(a) (preferably, p-methylstyrene).

20 [0018]

It is particularly preferred that the polymer block B is  
a polyisoprene block composed of isoprene units or a  
hydrogenated polyisoprene block in which some or all of the  
carbon-carbon double bonds originating from the isoprene units  
25 have been hydrogenated; a polybutadiene block composed of

butadiene units or a hydrogenated polybutadiene block in which  
some or all of the carbon-carbon double bonds originating from  
the butadiene units have been hydrogenated; or a copolymer  
block composed of isoprene units and butadiene units or a  
5 hydrogenated copolymer block in which some or all of the  
carbon-carbon double bonds originating from the isoprene units  
or the butadiene units have been hydrogenated.

[0019]

As long as the polymer block A and the polymer block B  
10 are linked to one another, they may be linked in any manner of  
linking, forming a straight-chained, branched or radial  
molecule of the addition polymerization-based block copolymer  
(a). Two or more of these manners of linking may be combined  
in one molecule. Preferably, the polymer block A and the  
15 polymer block B are linked together to form a straight-chained  
molecule. Examples of the straight-chained molecules include  
triblock copolymers as denoted by A-B-A, tetrablock copolymers  
as denoted by A-B-A-B and pentablock copolymers as denoted by  
A-B-A-B-A, given that "A" represents the polymer block A and  
20 "B" represents the polymer block B. Of these, triblock  
copolymers ("A-B-A") are particularly preferred because of  
their flexibility and readiness of the production of the  
addition polymerization-based block copolymer (a).

[0020]

25 While the block copolymer (I) for use in the present

invention may have any number average molecular weight, it preferably has a number average molecular weight in the range of 30000 to 1000000, and more preferably in the range of 40000 to 300000. The term "number average molecular weight" as used  
5 herein refers to a number average molecular weight as determined by gel permeation chromatography (GPC) using polystyrene standards.

[0021]

The addition polymerization-based copolymer (I) of the  
10 present invention can be produced, for example, by a known anionic polymerization technique. Specifically, the alkylstyrene for forming the structural unit (a), or a mixture of the alkylstyrene for forming the structural unit (a) and the aromatic vinyl compound, and the conjugated diene compound  
15 are sequentially polymerized to form a block copolymer (i.e., non-hydrogenated form of the addition polymerization-based block copolymer (I)). Using an initiator such as an alkylolithium compound, the reaction is carried out in n-hexane, cyclohexane, or other organic solvents that are inert to the  
20 polymerization.

When necessary, the resulting block copolymer is hydrogenated. The hydrogenation reaction is generally carried out in a saturated hydrocarbon solvent such as cyclohexane at a reaction temperature of 20 to 100°C under a hydrogen pressure  
25 of 0.1 to 10MPa and in the presence of a hydrogenation

catalyst, resulting in a hydrogenated product of the addition polymerization-based block copolymer (I). Examples of such hydrogenation catalysts include Raney nickels; non-uniform catalysts consisting of metals, such as Pt, Pd, Ru, Rh and Ni, carried by carbon, alumina, diatomite, and other suitable carriers; Ziegler catalysts consisting of an organic metal compound of, for example, nickel, cobalt, and other group VIII metals, combined with an organoaluminum compound or organolithium compound, such as triethylaluminum and triisobutylaluminum; and metallocene catalysts consisting of a bis(cyclopentadienyl) compound of transitional metals, such as titanium, zirconium, and hafnium, combined with an organic metal compound, such as lithium, sodium, potassium, aluminum, zinc, and magnesium.

[0022]

While the degree of hydrogenation may be adjusted depending on what physical properties are required of the polyolefin-based resin composition of the present invention, it is preferred that 70% or more, preferably 85% or more, and more preferably 95% or more of the carbon-carbon double bonds that result from the conjugated diene compound units of the polymer block B for forming the addition polymerization-based block copolymer (I) are hydrogenated when heat resistance, weather resistance, and ozone resistance are considered particularly important.



The degree of hydrogenation of the carbon-carbon double bonds that result from the conjugated diene compound units of the polymer block B can be determined by measuring the amount of the carbon-carbon double bonds in the polymer block B before the hydrogenation reaction and the amount after the hydrogenation reaction by means of iodimetry, IR spectrophotometry, nuclear magnetic resonance or other suitable techniques and taking the difference between these amounts.

10 [0023]

Examples of the polyolefin resin (II) for forming the polyolefin-based resin composition of the present invention include homopolymers, such as high density polyethylene (HDPE), middle density polyethylene, low density polyethylene (LDPE), and polypropylene; ethylene- $\alpha$ -olefin copolymers, such as ethylene-propene copolymer, ethylene-1-butene copolymer, ethylene-1-hexene copolymer, ethylene-1-heptene copolymer, ethylene-1-octene copolymer, ethylene-4-methyl-1-pentene copolymer, ethylene-1-nonene copolymer, and ethylene-1-decene copolymer; and ethylene-vinyl acetate copolymers, ethylene-acrylate copolymers, ethylene-methacrylic acid copolymers and ethylene-methacrylate copolymers, and resins obtained by modifying these copolymers with maleic anhydride or the like. Of these, high density polyethylene, middle density polyethylene, low density polyethylene, polypropylene,

ethylene-polypropylene copolymer, and ethylene- $\alpha$ -olefin copolymer are particularly preferred.

[0024]

Preferably, the polyolefin-based resin compound of the present invention contains the addition polymerization-based copolymer (I) and the polyolefin-based resin (II) at a mass ratio of the addition polymerization-based copolymer (I) to the polyolefin-based resin (II) of 90/10 to 1/99, more preferably, 80/20 to 20/80 and, still more preferably, 70/30 to 30/70. If the amount of the polyolefin-based resin (II) relative to the total mass of the addition polymerization-based block copolymer (I) and the polyolefin-based resin (II) is 10% by mass or less, or 99% by mass or more, then the resulting polyolefin-based resin composition does not exhibit flexibility, mechanical strength, heat resistance, and solvent resistance in a well-balance manner.

[0025]

In the polyolefin-based resin composition of the present invention, the active energy ray that is used to crosslink at least the part of the addition polymerization-based block copolymer (I) formed of the polymer block A may be a particle beam, electromagnetic wave, and combination of these. Examples of the particle beam include electron beam (EB) and  $\alpha$ -ray, and examples of the electromagnetic wave include ultraviolet ray (UV), visible light, infrared,  $\gamma$ -ray, and X-ray. Of these,

electron beam (EB) and ultraviolet ray (UV) are particularly preferred.

These active energy rays can be irradiated using known apparatuses. The electron beam may be accelerated at a voltage of 0.1 to 10MeV and irradiated at a dose of 1 to 500kGy. A lamp with an irradiation wavelength of 200 to 450 nm may be preferably used as the source of ultraviolet ray (UV). Examples of the electron beam (EB) source include tungsten filament, and examples of the ultraviolet ray (UV) source include low-pressure mercury-vapor lamp, high-pressure mercury-vapor lamp, ultraviolet mercury lamp, carbon arc lamp, xenon lamp, and zirconium lamp.

[0026]

When the active energy ray is irradiated to crosslink at least the part of the addition polymerization-based block copolymer (I) formed of the polymer block A in the polyolefin-based resin composition of the present invention, it is not only the part of the addition polymerization-based block copolymer (I) formed of the polymer block A that is crosslinked, but the part of the addition polymerization-based block copolymer (I) formed of the polymer block B and the polyolefin-based resin (II) is also partly crosslinked. However, such cross-linkages, if any, do not interfere with the objective of the invention.

[0027]

When necessary, and especially when ultraviolet ray (UV) is used as the active energy beam, a photopolymerization initiator is further added to the polyolefin-based resin composition of the present invention. Examples of such photopolymerization initiators include, but are not limited to, benzophenone, benzoin, benzoin methyl ether, benzoin ethyl ether, benzoin isopropyl ether,  $\alpha$ -methylolbenzoin,  $\alpha$ -methylolbenzoin methyl ether,  $\alpha$ -methoxybenzoin methyl ether, benzoin phenyl ether, and  $\alpha$ -t-butylbenzoin. These photopolymerization initiators may be used either individually or in combination of two or more photopolymerization initiators. While the photopolymerization initiator, when used, may be added to the polyolefin-based resin composition in any amount, it is preferably added in an amount of 0.01 to 5% by mass with respect to the total mass of the addition polymerization-based block copolymer (I) and the polyolefin-based resin (II).

[0028]

When necessary, a crosslinking aid is further added to the polyolefin-based resin composition of the present invention. Examples of such crosslinking aids include triallyl isocyanurate, N,N'-phenylenebismaleimide, ethylene glycol diacrylate, propanediol diacrylate, butanediol diacrylate, hexanediol diacrylate, and nonanediol diacrylate.

[0029]

When necessary, a softener is further added to the polyolefin-based resin composition of the present invention. Examples of such softeners include petroleum-based softeners, such as paraffin-, naphthene- or aromatic compound-based processed oils; paraffin; and vegetable oil-based softeners, such as peanut oil and rosin. These softeners may be used either individually or as a mixture of two or more softeners. While the softener, when used, may be present in any amount that does not interfere with the objective of the present invention, it is typically added in an amount of 300 parts by mass or less, preferably 100 parts by mass or less, with respect to 100 parts by mass of the addition polymerization-based block copolymer (I).

[0030]

A filler may be further added to the polyolefin-based resin composition of the present invention for the purpose of improving fillability, heat resistance, and rigidity of the composition. Examples of such fillers include talc, glass fiber, mica, kaolin, titanium oxide talc, clay, calcium silicate, glass, hollow glass sphere, calcium carbonate, magnesium carbonate, aluminum hydroxide, magnesium hydroxide, calcium aluminate, calcium hydroxide, zinc borate, dawsonite, poly-ammonium phosphate, hydrotalcites, silica, alumina, titanium oxide, iron oxide, zinc oxide, magnesium oxide, tin oxide, antimony oxide, barium ferrite, strontium ferrite,

carbon black, graphite, carbon fiber, activated carbon, hollow carbon sphere, calcium titanate, lead titanate zirconate, silicon carbide, wood filler, starch, organic pigments, polystyrene, poly p-methylstyrene and polyamide.

5 [0031]

Other additives may be added to the polyolefin-based resin composition of the present invention, including thermostabilizers, photostabilizers, UV-absorbents, antioxidants, lubricants, coloring agents, antistats, flame  
10 retardants, blowing agents, water repellants, waterproof agents, hydrophilicity-imparting agents, electroconductivity-imparting agents, heat conductivity-imparting agents, electromagnetic wave shield property-imparting agents, light transmittance conditioners, fluorescent agents, slidability-  
15 imparting agents, transparency-imparting agents, anti-blocking agents, metal-inactivating agents and antimicrobial agents.

[0032]

As long as the objective of the present invention is not affected, other elastomers may be added to the polyolefin-  
20 based resin composition of the present invention for the purpose of improving flexibility and fluidity. Examples of such elastomers include natural rubber, synthetic polyisoprene rubber, liquid polyisoprene rubber and hydrogenated products thereof, polybutadiene rubber, liquid polybutadiene rubber and  
25 hydrogenated products thereof, styrene-butadiene rubber,

chloroprene rubber, ethylene-propylene rubber, acrylic rubber,  
poly isoprene/isobutylene rubber, acrylonitrile-butadiene  
rubber, and styrene-based elastomers, such as polystyrene-  
polyisoprene-polystyrene block copolymer, polystyrene-  
5 polybutadiene-polystyrene block copolymer and hydrogenated  
products thereof.

[0033]

As long as the objective of the present invention is not  
affected, a thermoplastic polyester resin, polyamide resin,  
10 polyphenylene ether resin, or other reinforcing resins having  
a relatively small molecular weight may be added to the  
polyolefin-based resin composition of the present invention  
for the purpose of ensuring the balance between the heat  
resistance, solvent resistance, and other properties of the  
15 composition.

[0034]

Using a common tank-type mixer, high-speed stirrer,  
enclosed kneader, internal mixer or extruder, such as a single  
screw extruder and a twin screw extruder, the polyolefin-based  
20 resin composition of the present invention can be prepared by  
melting/mixing together the addition polymerization-based  
block copolymer (I), the polyolefin-based resin (II), and the  
optional photopolymerization initiator, softener and other  
optional components. The melting/mixing is carried out at  
25 130°C to 230°C and, when necessary, in a nitrogen atmosphere.

The resulting polyolefin-based resin composition may be formed into different forms depending on its intended applications and the manner of usage: it may be formed into blocks, granules, flakes, pellets, sticks, films, sheets, and other forms suitable for use in wire coatings, coatings of various cables, tubes, films, and sheets.

[0035]

Upon the stirring/mixing, maleic anhydride and a peroxide (such as dicumylperoxide, dicumylperoxide, di-t-butylperoxide, and 2,5-dimethyl-2,5-di(t-butylperoxy)hexane) may further be added. In this manner, one or both of the addition polymerization-based block copolymer (I) and the polyolefin-based resin (II) are modified with maleic anhydride, so that the resulting polyethylene resin composition acquires an ability to disperse the filler and/or an ability to form a multilayer structure with, or adhere to, a polar resin, such as polyamide, polycarbonate, polybutylene terephthalate, and polyethylene terephthalate.

[0036]

The polyolefin-based resin composition obtained in the above-described manner is then molded by various molding techniques, such as injection molding (e.g., insert molding, two-color molding, sandwich molding, and gas injection molding), extrusion molding, inflation molding, T-die film molding, laminate molding, blow molding, hollow molding,



compression molding, and calendering. Once molded/processed, the composition is irradiated with the active energy ray to form cross-linkages.

[0037]

- 5       The molded/processed articles can be used in films, such as food wrapping film and fiber wrapping film, processed paper, wire coatings, pipes, sheets, stationeries, food containers, daily commodities, and other applications.

[0038]

- 10       The so-obtained polyolefin-based resin composition is formed into a layer, which is laminated with a layer of other polyolefin resin, such as polypropylene, and when necessary, an adhesive layer or other layers to form a flexible laminate.

[0039]

- 15       An adhesive resin may be added to the polyolefin-based resin composition preferably in an amount of 1 to 500 parts by mass to make the composition adhesive. The resin is then molded into, for example, a film to serve as an adhesive film. Examples of such adhesive resins include rosin-based resins, 20   terpene-based resins, aliphatic petroleum resins, aromatic petroleum resins, alicyclic petroleum resins, coumarone and indene resins, styrene-based resins, alkylphenol resins, and xylene resins.

[0040]

- 25   [Examples]

The present invention will now be described in further detail with reference to examples, which are not intended to limit the scope of the invention in any way.

In each of Examples and Comparative Examples described below, an exemplary polyolefin-based resin composition was evaluated for its hardness, break strength, break elongation, and solvent resistance. The evaluation was made according to the following methods.

[0041]

10 1) Hardness

The hardness was measured according to the method described in JIS K 6253. Specifically, a sheet-like article (11cm x 11cm x 0.2cm) was prepared from one of the polyolefin-based resin compositions obtained in Examples and Comparative Examples and the hardness of the article was measured using an ASTM D hardness meter as an index of the flexibility.

[0042]

2) Mechanical strength

The mechanical properties were tested according to the method described in JIS K 6251. Specifically, two No. 5 dumbbell-shaped sample pieces were prepared, as specified in JIS K 6251, from a sheet-like article made of each of the polyolefin-based resin compositions of Examples and Comparative Examples. The two sample pieces were stretched on an INSTRON universal tester at a rate of 500mm/min, one at 23°C

and the other at 80°C, to determine the break strength (MPa) and the break elongation (%) for each sample piece.

[0043]

### 3) Deformation temperature

5       A No. 6 dumbbell-shaped sample piece as specified by JIS K 6251 was prepared from a sheet-like article made of one of the polyolefin-based resin compositions obtained in Examples and Comparative Examples. The sample piece was suspended in an oven while a 72g load was applied. The temperature in the oven  
10       was then raised at a rate of 3°C/min to the point at which the sample piece was stretched by 100%. This temperature was measured as an index of the heat resistance of the composition.

[0044]

### 4) Toluene extraction rate

15       A part of a pre-weighed dumbbell-shaped sample piece for stretch test (approx. 0.3g) was placed in 30ml toluene in a 50ml screw tube. The tube was then agitated on an agitator at 25°C for 12 hours. Subsequently, the sample piece was taken  
20       out from the tube, was dried at 100°C for 180 minutes under a reduced pressure, and was weighed. The toluene extraction rate was determined by the following equation from the weight of the dried sample piece. The toluene extraction rate so  
obtained serves as an index of the solvent resistance of the composition.

25       Toluene extraction (%) =  $100 \times (A_0 - A_1) / A_0$

where  $A_0$  = mass (g) of the sample piece prior to agitation in toluene; and  $A_1$  = mass (g) of the sample piece following agitation in toluene and subsequent drying.

[0045]

5 Reference Example 1

39kg cyclohexane and a 180ml cyclohexane solution of sec-butyl lithium (11% by mass) were placed in a pressure vessel equipped with a stirrer. To this solution, 1.32kg of a mixture of p-methylstyrene and styrene (p-methylstyrene/styrene = 10 50/50 (by mass)) were added over a 30-minute period and the polymerization was allowed to proceed at 50°C for 60 minutes. Subsequently, 10.7kg of a mixture of isoprene and butadiene (isoprene/butadiene = 50/50 (by mass)) were added over a 60-minute period and the polymerization was allowed to proceed at 15 50°C for 90 minutes. Additional 1.32kg of the mixture of p-methylstyrene and styrene (p-methylstyrene/styrene = 50/50 (by mass)) were added over a 30-minute period and the polymerization was allowed to proceed at 50°C for 60 minutes. This gave a reaction mixture containing a poly(p- 20 methylstyrene/styrene)-poly(isoprene/butadiene)-poly(p-methylstyrene/styrene) triblock copolymer (which is referred to as 'block copolymer (I)-1, hereinafter'). The resulting block copolymer (I)-1 had a number average molecular weight of 94000, and the total amount of p-methylstyrene and styrene as 25 determined by  $^1\text{H-NMR}$  was 20% by mass.

To the resulting reaction mixture containing the block copolymer (I)-1, a hydrogenation catalyst, which was separately prepared by adding 380g of triisopropylaluminum (20% by mass, cyclohexane solution) to 56g of nickel octanoate (64% by mass, cyclohexane solution), was added, and the hydrogenation reaction was allowed to proceed at 80°C in a hydrogen atmosphere of 1MPa. This gave a hydrogenated product of the poly(p-methylstyrene/styrene)-poly(isoprene/butadiene)-poly(p-methylstyrene/styrene) triblock copolymer (The product is referred to as "block copolymer (I)-2," hereinafter). The resulting block copolymer (I)-2 had a number average molecular weight of 100000, and the total amount of p-methylstyrene and styrene and the degree of hydrogenation as determined by <sup>1</sup>H-NMR were 19% by mass and 97%, respectively.

[0046]

#### Reference Example 2

39kg cyclohexane and a 180ml cyclohexane solution of sec-butyl lithium (11% by mass) were placed in a pressure vessel equipped with a stirrer. To this solution, 1.32kg of styrene were added over a 30-minute time period and the polymerization was allowed to proceed at 50°C for 30 minutes. Subsequently, 10.7kg of a mixture of isoprene and butadiene (isoprene/butadiene = 50/50 (by mass)) was added over 60 minutes and the polymerization was allowed to proceed at 50°C for 90 minutes. This was followed by the addition of 1.32kg of

styrene over a 30-minute period and subsequent polymerization at 50°C for 60 minutes. This gave a reaction mixture containing a polystyrene-poly(isoprene/butadiene)-polystyrene triblock copolymer (which was referred to as 'block copolymer (I)-3,' hereinafter). The resulting block copolymer (I)-3 had a number average molecular weight of 94000, and the amount of styrene as determined by <sup>1</sup>H-NMR was 20% by mass.

To the resulting reaction mixture containing the block copolymer (I)-3, a hydrogenation catalyst, which was separately prepared by adding 380g of triisopropylaluminum (20% by mass, cyclohexane solution) to 56g of nickel octanoate (64% by mass, cyclohexane solution), was added, and the hydrogenation reaction was allowed to proceed at 80°C in a hydrogen atmosphere of 1MPa. This gave a hydrogenated product of the polystyrene-poly(isoprene/butadiene)-polystyrene triblock copolymer (The product is referred to as 'block copolymer (I)-4,' hereinafter). The resulting block copolymer (I)-4 had a number average molecular weight of 100000, and the amount of styrene and the degree of hydrogenation as determined by <sup>1</sup>H-NMR were 19% by mass and 97%, respectively.

[0047]

#### Examples 1 through 4

In each of Examples 1 through 4, a polyolefin-based resin composition was obtained by melting and mixing the following components on a twin screw extruder: the block copolymer (I)-2

obtained in Reference Examples 1; a polyolefin-based resin  
 [PE1 = NOVATEC LD EH30 (a low-density polyethylene  
 manufactured by Japan Polychem Corporation, MFR (190°C, 2.16kg  
 load)= 2.0g/10min), PE2 = ULTZEX 1520L (a linear low-density  
 5 polyethylene manufactured by Mitsui Chemicals Co., Ltd., MFR  
 (190°C, 2.16kg load)= 2.3g/10min)]; and an antioxidant. These  
 components were melted and mixed at 200°C in respective  
 proportions (by mass) shown in Table 1 below to give the  
 polyolefin-based resin compositions of Examples 1 through 4.  
 10 Each of the resulting polyolefin-based compositions was used  
 to make a sheet sized 15cm x 15cm x 0.1cm. The sheet was then  
 irradiated with an electron beam accelerated at a voltage of  
 5.0MeV and were irradiated at a dose of 200kGy. The resulting  
 sheets of the respective polyolefin-based resin compositions  
 15 were evaluated for the different performances in the manner  
 described above. The results are shown in Table 1 below.

[0048]

Comparative Examples 1 through 4

The same polyolefin-based resin compositions as those  
 20 used in Examples 1 through 4 were used to make sheet-like  
 articles, which were processed in the same manner as in  
 Examples 1 through 4, respectively, without electron beam  
 irradiation, and were evaluated for the different performances.  
 The results are shown in Table 1 below.

25 [0049]

Comparative Examples 5 through 8

In Comparative Examples 5 through 8, sheets were prepared from respective polyolefin-based resin compositions in the same manner as in Examples 1 through 4, respectively, while  
5 using the block copolymer (I)-4 obtained in Reference Examples 2, and were evaluated for the different performances. The results are shown in Table 1.



[0050]

[Table 1]

	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4	Comp. Ex. 5	Comp. Ex. 6	Comp. Ex. 7	Comp. Ex. 6
(I) Addition polymerization-based block copolymer												
(I)-2	20	20	50	50	20	20	50	50				
(I)-4									20	20	50	50
(II) Polyolefin resin												
PE1	80		50		80		50		80		50	
PE2		80		50		80		50		80		50
Antioxidant: Irganox 1010	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Hardness (Type D)	31	33	24	27	32	34	21	28	31	34	26	26
Break strength (23°C, MPa)	25	32	26	33	16	31	32	33	23	29	28	32
Break elongation (23°C, %)	530	570	510	540	570	590	540	500	550	570	580	580
Break strength (80°C, MPa)	6.9	12	5.1	6.5	2.9	8.3	2.1	3.3	7.3	11	4.3	5.8
Break elongation (80°C, %)	480	690	550	620	240	800	200	590	550	690	560	630
Deformation temperature (°C)	238	242	222	238	94	100	92	96	128	220	136	192
Toluene extraction (%)	0	0	0	5	16	14	34	31	0	0	7	7

Irganox 1010: Product Name, Ciba Specialty Chemicals Co., Ltd.; Hindered phenol-based

antioxidant

[0051]

The results of Tables 1 indicate that the molded articles formed of the polyolefin-based resin compositions of Examples 1 through 4 exhibit superior mechanical strength, higher heat resistance, and higher solvent resistance as compared to the corresponding non-irradiated, non-crosslinked molded articles of Comparative Examples 1 through 4.

The results also indicate that the molded articles formed of the respective polyolefin-based resin compositions of Examples 1 through 4 are more favorable in terms of their mechanical strength, heat resistance and solvent resistance at higher temperatures as compared to the corresponding molded articles of the respective polyolefin-based resin compositions of Comparative Examples 5 through 8, each of which includes a block copolymer having its hard segment formed of blocks composed solely of styrene units.

[0052]

[Advantages of the Invention]

As set forth, the present invention provides a polyolefin-based resin composition that not only has flexibility, but also exhibits mechanical strength, heat resistance, and solvent resistance in a well-balanced manner.

[Document Name]            Abstract

[Summary]

[Object]     To provide a polyolefin-based resin composition  
that not only has flexibility, but also exhibits mechanical  
5   strength, heat resistance, and solvent resistance in a well-  
balanced manner.

[Solution]   A polyolefin-based resin composition contains an  
addition polymerization-based block copolymer (I) and a  
polyolefin-based resin (II), wherein: the addition  
10   polymerization-based block copolymer (I) comprises at least  
one polymer block A and at least one polymer block B, the  
polymer block A essentially comprises an aromatic vinyl  
compound containing at least 1% by mass of an alkylstyrene-  
derived structural unit (a) in which at least one alkyl group  
15   having 1 to 8 carbon atoms is bound to a benzene ring, the  
polymer block B essentially comprises a conjugated diene  
compound unit; at least the part of the addition  
polymerization-based block copolymer (I) formed of the polymer  
block A comprises at least one selected from the group  
20   consisting of block copolymers that can undergo crosslinking  
upon exposure to an active energy ray and hydrogenated  
products thereof; and after molded into a desired shape, the  
composition is exposed to an active energy ray to carry out  
the crosslinking reaction.

25   [Selected Drawing]        None